Development of a New Fundamental Equation for Natural Gases Covering the Gas and Liquid Region Including the Phase Equilibrium

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As part of a research project which is being carried out in cooperation with companies of the European natural gas industry, we are working on a new equation of state for the thermodynamic properties of natural gases covering the gas and liquid region including the phase equilibrium gas-liquid.

The formulation is a fundamental equation that is explicit in the reduced Helmholtz free energy. The independent variables are density, temperature, and composition. Similar to existing mixture models, we calculate the Helmholtz free energy as the sum of the ideal gas contribution, a contribution from the pure fluid equations combined at the reduced temperature and the reduced density of the mixture, and a departure function. The reducing functions used for temperature and density depend on the mole fraction x. The new equation of state should allow the properties of typical natural gases to be calculated with the highest possible accuracy. The uncertainty in density and speed of sound at typical pipeline conditions should be less than \pm 0.1%. Due to the data situation, the description of the liquid phase will be less accurate, but clearly more accurate than achievable with the equations used for liquefied natural gas applications today. The new mixture model will also allow a reasonable description of properties in vapor-liquid equilibrium. Again, the limitations depend mainly on the available data base.

Besides the data available from literature, the model will be based on results of recent measurements of the density, speed of sound, and VLE properties carried out within the same project. New equations of state have been developed for the pure components in order to take into account the special needs resulting from a natural gas equation for technical applications. The mixture equation has been developed by using data for thermal and caloric properties of binary mixtures. The structure of the departure functions has been determined with a linear optimization procedure using data in the homogeneous region and in the vapor-liquid phase equilibrium. The reducing functions contain binary parameters, which have been fitted to selected data of thermodynamic properties of the respective binary mixture.